Freeze-foaming: A promising method for synthesizing cellular ceramic materials

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1 Introduction

Due to their characteristics, porous ceramic or metallic structures are a promising class of materials for lots of different and highly specified applications. Compared to relatively dense and heavy materials they are becoming more and more common in lightweight airplane or automobile construction manufacture. High inner surface and specific pore morphology make lots of fluidal flow and adsorption-desorption processes possible. Thus cellular structures are used for instance as particle filters, heat exchanger or SOFC. The additional possibility of open and interconnected pores of different pore size justifies even the use of biocompatible material and implants.

The typical and industrial widely used production methods (Replica Technique and Placeholder Method) are bound to an intermediate process step in which a polymer scaffold or other volatile pore fillers have to be burned out leaving the negative porous imprint behind [1-4]. An alternative approach without this intermediate step is the so called direct foaming technique. The cellular structure is developed either through gas injection or evolving gas due to chemical reactions or mechanical treatment of the liquid slurry [5-7]. Now, the so called freeze-foaming derives from the direct foaming. Dense struts and resulting mechanical improved properties as well as open porosity accompany a typical freeze foamed structure (Fig.1).

This promising approach comprises the environmentally friendly and energy saving foaming of an aqueous ceramic suspension containing few organic additives and the later freeze drying to a stable green body in just a few minutes. With just the thermal treatment thereafter the ceramic porous material is ready to be used for various applications.

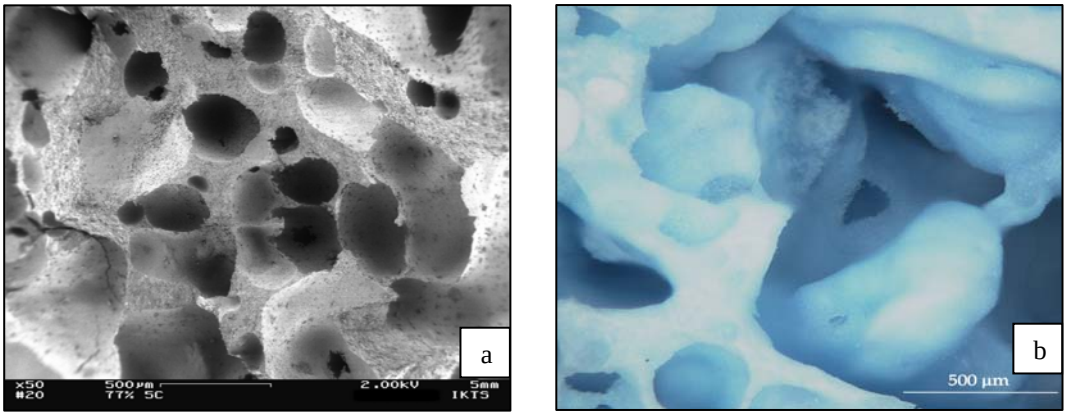

Figure 1: a) FESEM image of a sintered alumina foam structure made by freeze foaming, b) light microscopic image of a sintered freeze foamed hydroxyapatite structure

2 Experimental

To achieve reasonable freeze foamed structures the manufacturing procedure starts with the mixing of a homogeneous ceramic suspension. Studies with 35-60 vol.-% of varying powders (alumina, zirconia, hydroxyapatite, SiC) and 2 to 11 wt-% of organic additives were executed (see Fig.2). Organic aids are necessary as dispersants, temporary binders and foam stabilizers. The resulting suspension was mechanically stirred in an ultrasonic bath.

Afterwards, the homogeneous suspension is ready to be cast into an application-required mould of silicon rubber followed by the freeze-foaming step in a freeze dryer (Gamma-20, Martin Christ GmbH, Osterode).

Figure 2: sintered freeze-foamed structures, a) Al_2O_3, b) SiC, c) hydroxyapatite

2.1 The freeze-foaming process

The main step is the decompression of the ceramic suspension in the vacuum chamber of the freeze drying device. Due to the reduced ambient pressure the vapour partial pressure and the inflation of the entrapped air act as driving forces for the foaming process. Regarding the typical p, T – phase diagram of water, a pressure drop causes an automatic cooling of the whole system; in this case to the abrupt freezing of the foamed aqueous ceramic suspension as soon as the triple point is passed.

Now, a further pressure reduction leads to a further decrease in temperature. At a certain vacuum pressure the freeze drying device starts heating its panels and thus provides the sublimation energy for the freeze-drying process. Due to the porous structure of the foam and its huge surface drying takes place in only a few minutes. The dried foam can now be removed from the freeze drier and sintered to final ligaments density for attaining the final mechanical properties of the foam structure.

3 Characterization and Discussion

For this study the morphological characterization of the porous structures succeeded through complementary analysis at macroporous and microporous range.

The macroporous range is defined via the computed tomography. The resulting computed tomographic cross section images were binarized, segmented and structural values determined (Fig.3).

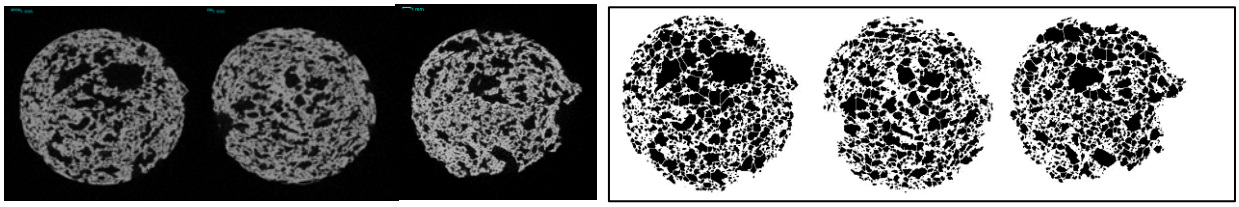

Figure 3: CT-cross section images (left) and resulting binarized and segmented foam images (right).

Thus, pore size and distribution as well as additional information about pore shape and elongation were obtained. To reach also the structural values of micro pores the Hg-porosimetry was executed. A resolution down to 1 µm is easy to achieve by this method (see Fig. 4).

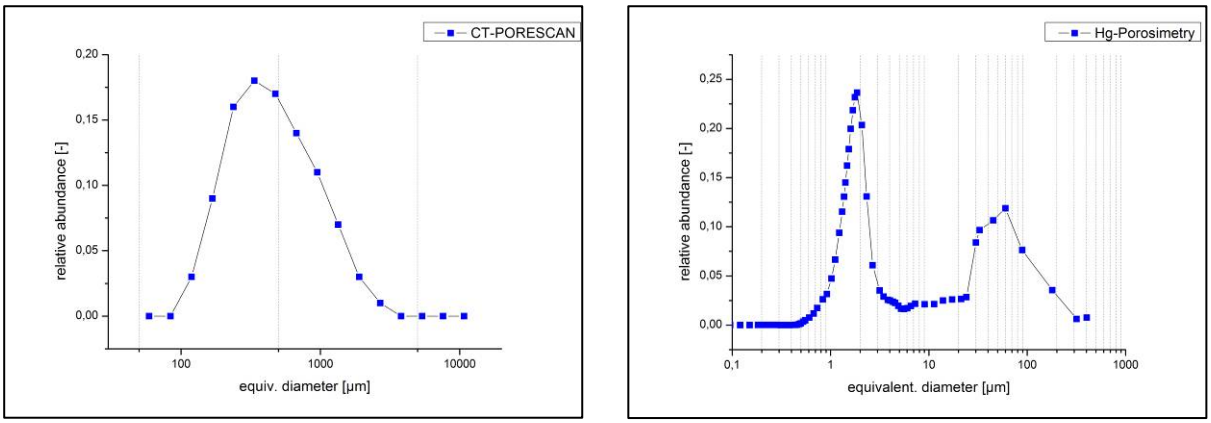

Figure 4: Pore distribution analysis via computed tomographic cross section images (left) and Hg-porosimetry (right).

Thus, using both range dependent morphological analyzing methods a more sophisticated conclusion about the cellular structure of foams is possible. Open and nano porosity as well as dense struts are observable by looking at FESEM images of selected ceramic structures (Fig. 5, Fig.6).

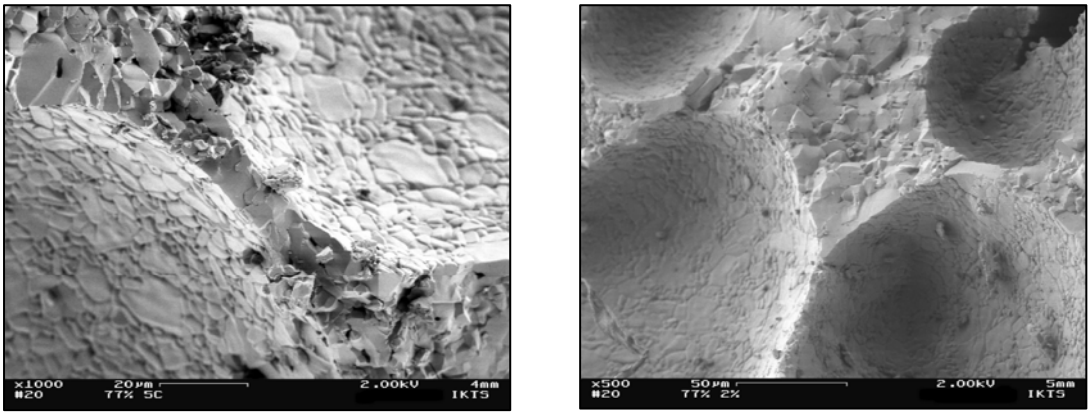

Figure 5: FESEM images of a sintered alumina foam showing dense struts

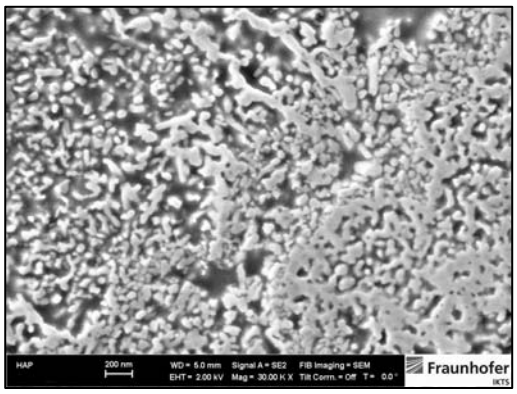

Figure 6: FESEM image of a sintered alumina foam showing nano porosity.

4 Conclusion

This study showed that the freeze foaming, as a novel approach to cellular structures, is a promising alternative way to create ceramic foams in an environmentally friendly and energy saving matter. Added to the possibility of foaming almost all ceramic and even metallic powders this promising technique assures benefit for lots of varying applications like bone scaffolds or thermally insulating materials.

5 References

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